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PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NIKKO KINZOKU KK

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(72)Inventor : ONO TOSHIYUKI
MORI MASAZUMI

(54) BASE STOCK FOR FE-NI ALLOY SHADOW MASK

(57)Abstract:

PURPOSE: To develop base stock for a Fe-Ni alloy shadow mask of which the punching property by etching can be largely improved.

CONSTITUTION: This base stock for a Fe-Ni alloy shadow mask consists of 30-50wt.% Ni and the balance Mn, Fe and inevitable impurities. In this material, amts. of Mn and S are specified to $\leq 0.05\text{wt.}\%$ and $\leq 0.005\text{wt.}\%$, respectively, and the amt. of Mn is ≥ 5 times as much as the amt. of S. It is preferable that among the inevitable impurities, C and Si each is included by $\leq 0.01\text{wt.}\%$. The cross-sectional cleanliness concerning to oxide inclusions measured by the method specified by JIS G 0555 is specified to $\leq 0.005\%$. The Figure indicates that the increasing rate of the etch factor largely changes from the line of 0.05wt.% Mn content. By specifying the amt. of Mn to ≥ 5 times as the amt. of S, the obtd. base stock can be processed to desired thickness without cracks.

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CLAIMS

[Claim(s)]

[Claim 1] nickel: The material for Fe-nickel system alloy shadow masks characterized by having contained 30 - 50wt%, and having regulated Mn less than [S:0.005wt%] in 0.05% or less and the unescapable impurity in the material for Fe-nickel system alloy shadow masks which the remainder becomes from Mn, Fe, and an unescapable impurity, and making Mn content into 5 or more times of S content.

[Claim 2] The material for Fe-nickel system alloy shadow masks of the claim 1 characterized by being less than [C:0.01wt%] and less than [Si:0.01wt%] in an unescapable impurity.

[Claim 3] JIS G Material for Fe-nickel system alloy shadow masks of the claim 1 characterized by the cross-section cleanliness of the oxide system inclusion measured by the method specified to 0555 being 0.05% or less, or a claim 2.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the material for Fe-nickel system alloy shadow masks which is especially excellent in etching punching nature about the material for Fe-nickel system alloy shadow masks used for the color-television Braun tube.

[0002]

[Description of the Prior Art] The shadow mask is used for the color-television picture tube as an electrode for color sorting. Recently, the Fe-nickel system alloy containing 30-50wt%nickel which has a low-thermal expansion property, especially the Fe-36wt%nickel system alloy are used more often as this charge of shadow mask material. Since this has a small thermal expansion accompanying the temperature rise of the shadow mask by bombardment [an electron beam / front faces other than the aperture of a shadow mask] compared with the low carbon aluminum killed steel used conventionally in the case of a Fe-nickel system alloy, it is because the fall of color purity is small.

[0003] However, it poses a problem that the Fe-nickel system alloy represented by this Fe-36wt%nickel system alloy is inferior to etching punching nature compared with a low carbon aluminum killed steel. A material with the big value called etch factor showing the ratio of an etch rate parallel to the etch rate and rolling side of the direction of board thickness of a shadow mask is needed, and development of the much more good material of etching punching nature is desired, so that the aperture of a shadow mask makes it highly minute especially. In addition, the above-mentioned etch factor EF is defined by $EF=d/SE$ as shown in drawing 3. d is the etching depth here, when R and the diameter of resist opening are set to r for the etching processing aperture which SE is the amount of side etch and was actually formed, it is expressed with $(R-r)/2$, and the amount in which the resist opening border was exceeded and the surplus *****ed in the direction of a plate surface is expressed.

[0004] On the other hand, although the method of improving etching punching nature by reduction of a nonmetallic inclusion or a minute amount impurity from the former was proposed, the improvement in etching punching nature was not what can fully be satisfied. moreover, in becoming the dry area of an etching side, and the cause of a stripe pattern, although the improvement of etching punching nature is aimed at at

JP,2-9654,B or JP,5-140698,A by giving strong processing and raising the degree of set of the {100} crystal faces to a rolling side -- etching processing -- the evil in which the configuration of a hole will lose roundness had arisen

[0005]

[Problem(s) to be Solved by the Invention] Offer of the quality shadow mask material which can respond to highly minute-ization of a shadow mask enough is demanded. The technical problem of this invention is developing the material for shadow masks which can improve sharply the etching punching nature of the Fe-nickel system alloy represented by the old Fe-36wt%nickel system alloy by the time it can respond to highly minute-ization enough, without producing the evil mentioned above.

[0006]

[Means for Solving the Problem] this invention is based on having found out that the degree of influence of Mn to an etch factor changed a lot bordering on Mn content =0.05wt% as a result of repeating various examination in view of the above-mentioned actual condition. In detail, like C and Si that whose etching punching nature is barred it is common knowledge, Mn is in the inclination which gets worse etching punching nature, when a content increases. An inverse proportion relation between the logarithm of these contents and an etch factor is, and while Mn content decreases by 1 figure like [Mn content / in the field beyond 0.05wt%] C or Si, an etch factor only increases 1.5 to 2%. However, it became clear that the rate of increase of an etch factor when Mn content decreases [Mn content] by 1 figure in the field not more than 0.05wt% has the large rate of increase of an etch factor rather than it becomes 5% or more and Mn content can set to the field beyond 0.05wt%. The standard content of Mn of the Fe-nickel system alloy represented by the Fe-36wt%nickel system alloy is 0.2 - 0.3wt% until now, therefore needs to lower Mn content to improving etching punching nature sharply less than [0.05wt%]. Although it was added in order for Mn to make harmless a bad influence, such as spoiling the hot-working nature of S which exists as an unescapable impurity, the bird clapper was found out regulating the relation between the amount of Mn, and the amount of S, i.e., by making Mn content into 5 or more times of S content, without spoiling hot-working nature as processing is possible to desired thickness.

[0007] Based on the above knowledge, the material for Fe-nickel system alloy shadow masks characterized by for this invention having contained nickel:30 - 50wt%, and having regulated Mn less than [S:0.005wt%] in 0.05% or less and the unescapable impurity in the material for Fe-nickel system alloy shadow masks which the remainder becomes from Mn, Fe, and an unescapable impurity, and making Mn content 5 or more times of S content is offered. Moreover, in an unescapable impurity, it considers as less

than [C:0.01wt%] and less than [Si:0.01wt%], and is JIS. G It is desirable that the cross-section cleanliness of the oxide system inclusion measured by the method specified to 0555 is 0.05% or less.

[0008]

[Function] The feature of the material for shadow masks of this invention is combined with the content of S, limits the content of Mn, and it raises etching punching nature, avoiding problems, such as hot-working nature which originates in S by specifying the relation between Mn content and S content further. Furthermore, in a much more desirable mode, you may be less than [C:0.01wt%] and less than [Si:0.01wt%] in an unescapable impurity. The relation between Mn, S and C, the content of Si each element, and etch-factor rate-of-change ΔEF is shown in drawing 1. In drawing 1, S is based on the etch factor at the time of 0.01wt(s)% for C and Si by Mn on the basis of the etch factor at the time of 0.005wt(s)% on the basis of the etch factor at the time of 0.25wt(s)% ($\Delta EF=0\%$). Mn of which the next relation consists between the content X of these elements, and etch-factor rate-of-change ΔEF : (when it is less than [0.05wt%])

$$\Delta EF = -5.52 - 5.75 \times \log(X)$$

(in the case of beyond 0.05wt%)

$$\Delta EF = -0.91 - 1.48 \times \log(X)$$

$$C : \Delta EF = -3.80 - 1.90 \times \log(X)$$

$$Si : \Delta EF = -3.48 - 1.74 \times \log(X)$$

$$S : \Delta EF = 8.71 + 3.79 \times \log(X)$$

In drawing 1, although it has the straight-line relation of inclination with fixed Content X and etch-factor rate-of-change ΔEF , as for the case of C and Si, in the case of Mn, it turns out that linear inclination is changing rapidly bordering on 0.05wt%. That is, while Mn content decreases by 1 figure like [Mn content / in the field beyond 0.05wt%] C or Si, an etch factor only increases 1.5 to 2%. However, it turns out that the rate of increase of an etch factor when Mn content decreases [Mn content] by 1 figure in the field not more than 0.05wt% becomes 5% or more, and the rate of increase of an etch factor increases sharply rather than Mn content can set to the field beyond 0.05wt%. C: By considering as less than [0.01wt%] and less than [Si:0.01wt%], an etch factor is further improvable.

[0009] Next, the relation between the cross-section cleanliness of oxide system inclusion and etch-factor rate-of-change ΔEF is shown in drawing 2. It is based on the etch factor in case cross-section cleanliness is 0.05% ($\Delta EF=0\%$). : of which the next relation consists between the cross-section cleanliness Z and etch-factor rate-of-change ΔEF : $\Delta EF = -0.33 - 0.26 \times \log(Z)$

Compared with the influence the content of the element of drawing 1 affects etch-factor rate of change, it turns out that the influence the cross-section cleanliness of oxide system inclusion affects etch-factor rate of change is small 1 figure. That is, if the etch-factor rate of change when reducing the time of reducing Mn content from 0.05wt(s)% to 0.01wt(s)% and cross-section cleanliness from 0.05wt(s)% to 0.01wt(s)% is compared, the direction in the case of Mn content will become large 20 or more times.

[0010] In addition to high intensity, moderate thermal resistance, and corrosion resistance, the Fe-nickel system alloy containing 30-50wt%nickel has a low-fever expansion property. When nickel is less than [30wt%], such an outstanding property is not fully discovered. Moreover, in exceeding 50wt(s)%, a low-fever expansion property is lost and it becomes expensive again. In less than [0.05wt%], the more there is little : (1) Mn:Mn which explains the reason for limitation of each element for participating in below, the more it can raise an etch factor remarkably. However, the amount of 5 times or more of S content is [to make it not spoil hot-working nature] required, since S of an unescapable impurity exists to make S harmless. For this reason, the content of Mn is made $5 \times S \text{ content} \leq \text{Mn content} \leq 0.05\text{wt}\%$.

(2) Although little C:C is so desirable that there is in order to check etching punching nature, it is difficult from a viewpoint of economical efficiency to reduce C sharply on a scale of industrial. therefore, the upper limit of C content -- 0.01wt(s)% -- it carries out to 0.005wt(s)% preferably

(3) Although little Si:Si is so desirable that there is in order to check etching punching nature, it is difficult from a viewpoint of economical efficiency to reduce Si sharply on a scale of industrial. therefore, the upper limit of Si content -- 0.01wt(s)% -- it carries out to 0.005wt(s)% preferably

(4) It has the operation which enlarges an etch factor as the content of S:S increases. However, the fewer one is desirable, when there is no element which makes S, such as Mn, harmless, in order to check hot-working nature. However, it is difficult from a viewpoint of economical efficiency to reduce S sharply on a scale of industrial. Therefore, the upper limit of S content is made 0.005wt(s)%.

(5) Oxide system inclusion : what is necessary is just to reduce the degree of contribution to the improvement in an etch factor to a grade with the existence substantially acting as [grade] the obstacle of etching compared with an above-mentioned element, since it is small, although little oxide system inclusion is so desirable that there is in order to check etching punching nature. It is JIS about this upper limit. G It will become 0.05% if expressed with the cross-section cleanliness for which it asked by the measuring method specified to 0555.

[0011] Next, the manufacture method is described. this invention makes Mn content less than [0.05wt%], and this is possible by adding the addition of Mn at the time of dissolving a Fe-nickel system alloy so that it may become 0.05wt(s)%, satisfying the requirements of 5 times or more of S content, and can be performed by the dissolution method of common knowledge, such as vacuum melting and the air dissolution. However, if a dissolution raw material is selected carefully and there is need in order to make C, Si, and S below into the amount of specification, it is desirable to perform deoxidation, decarbonization, and desulfurization processing. Moreover, it is desirable to make into 0.05% or less cross-section cleanliness (for it to measure by the method specified to JIS G 0555) of oxide system inclusion. It is obtained when this also fully performs deoxidation, decarbonization, and desulfurization processing. Much more good etching punching nature is obtained by reducing C, Si, and oxide system inclusion which check etching punching nature below in predetermined proportion. Ingot making of the molten metal may carry out continuous casting rather than it may be carried out. Thus, it can forge, or the obtained ingot can be rolled out, without starting hot shortness, and the material for shadow masks of desired thickness can be obtained by repeating annealing and cold rolling.

[0012] It is desirable to adjust the degree of preforming so that it may become 60 - 85% based on the value calculated with a formula 1 about the degree of integration of the {100} crystal faces in the rolling side after the last cold working. Much more improvement of etching punching nature can be aimed at.

[0013]

[Equation 1]

[0014] Thus, according to this invention, the material for shadow masks which improved sharply the etching punching nature at the time of etching, especially the etch

factor for the first time can be manufactured by limiting the content of S and Mn of a Fe-nickel system alloy to below the amount of specification, respectively, and specifying the relation between Mn content and S content. In addition, much more good etching punching nature is obtained by reducing the content of C and Si and/, or cross-section cleanliness.

[0015]

[Example] Below, an example and the example of comparison are shown. Sample No.1-8 are an example with which the requirements for this invention are filled, and sample No.9-18 are an example of comparison. Although sample No.9-10 have few Mn contents among the examples of comparison, Mn content is a less than 5 times [of S content] thing, Mn content of sample No.11-15 exceeds 0.05wt(s)%, one content of C and Si of sample No.16-17 exceeds 0.01wt(s)%, and, as for sample No.18, S content exceeds 0.005wt(s)%.

[0016] The ingot which adjusted the content of Mn, C, S, and Si of a Fe-36wt%nickel alloy and the cross-section cleanliness of oxide system inclusion by the vacuum melting process was obtained. Next, forging rolling was carried out, cold rolling and annealing were repeated, and the alloy band of 0.15mm thickness was manufactured. At this time, with the value expressed with a formula 1 in the degree of integration of the {100} crystal faces in the rolling side after the last cold working, the degree of preforming was adjusted so that it might become 60 - 85%. In order to compare the etching punching nature of these alloy bands, well-known photo lithography technology was used, the resist mask which has much openings on the perfect circle whose diameter is 80 micrometers was formed in the front face of one side of an alloy band, and the etch factor when the amount of side etch which sprays a ferric chloride solution in the shape of a spray, and is shown in drawing 3 is set to 15 micrometers was investigated. Moreover, generating of the crack at the time of hot working was evaluated as hot-working nature. These results in an example and the example of comparison are collectively shown in Table 1.

[0017]

[Table 1]

[0018] The result of Table 1 shows that the etch factor is large 0.1 or more compared with that to which, as for the following [0.05wt%], Mn content of sample No.11-13 exceeds [Mn content of sample No.1-8 of this invention] 0.05wt(s)%. Although sample No.9-10 have few Mn contents, since Mn content is less than 5 times of S content, the crack at the time of hot working has been produced. Furthermore, although C, Si, or S of sample No.16-18 is contained exceeding the amount of specification, since there is

almost no fall of an etch factor, by reducing Mn content shows that an etch factor can be improved sharply for the first time. although an etch factor will become large here if S content is made [many] -- aggravation of hot-working nature, and etching processing -- since the defect of shape of a hole is produced, it is unsuitable as a material for shadow masks Moreover, it can be processed even 0.15mm thickness, without producing the crack at the time of hot working because Mn content makes it 5 or more times of S content.

[0019]

[Effect of the Invention] As stated above, according to this invention, in the material for Fe-nickel system alloy shadow masks, it is limiting Mn and S to below a predetermined value, and specifying the relation between Mn content and S content, and limiting the content of C and Si, and/or the cross-section cleanliness of oxide system inclusion to below a predetermined value still more desirably, and made it possible to offer the material for shadow masks excellent in etching punching nature. Offer of the quality shadow mask material corresponding to highly-minute-izing of a shadow mask is attained enough by this, and the industrial meaning is very large.

[Translation done.]